

Supporting Information:

# Stabilizing Single Sites on Solid Supports: Robust Grafted Ti(IV)-Calixarene Olefin Epoxidation Catalysts via Surface Polymerization and Crosslinking

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## Supporting information

### Materials and General Methods.

Mesoporous SiO<sub>2</sub> (Selecto Scientist) support consists of a 32-63  $\mu\text{m}$  silica particle size, possesses a N<sub>2</sub> BET surface area of 498 m<sup>2</sup>/g, and produces pH  $\sim$  7 as a 5% suspension in H<sub>2</sub>O

(0.877 mol/L). Before being used as a catalyst support, the mesoporous SiO<sub>2</sub> was dehydroxylated in a quartz Schlenk tube at 800 °C for 4 h by flowing a mixture of dry air and Ar, and was subsequently stored in a N<sub>2</sub>-filled glovebox prior to use. The resulting hydroxylated material is denoted as SiO<sub>2</sub>@800. Toluene (Aldrich) and octane (Aldrich) were freshly distilled over Na prior to use. Styrene ( $\geq 99\%$ , Aldrich) and 1,3-diisopropenylbenzene (97%, Aldrich) were passed through a basic Al<sub>2</sub>O<sub>3</sub> column, dried with CaH<sub>2</sub>, and purified via vapor transfer. B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> ( $\geq 95\%$ , Aldrich), Ti(O<sup>*i*</sup>Pr)<sub>4</sub> (97%, Aldrich) and poly(tetrafluoroethylene) (powder, Aldrich) were used as received.

The content of grafted organic species (i.e. grafted calixarene ligands and their polymerized derivatives) in catalysts was determined by thermogravimetric analysis (TGA; Netzsch 449C Jupiter TGA) in a mixed gas flow consisting of 20% O<sub>2</sub> and 80% Ar. The temperature program consists of: (i) heating at 5 °C/min to 120 °C and holding for 60 min and (ii) heating at 5 °C/min up to a final temperature of 800 °C. Ti loadings in the catalysts were measured using a UV-Vis spectrophotometric technique as previously described,<sup>27</sup> along with confirmatory ICP/MS<sup>17,18</sup> for Ia and IIa. The spectrophotometric technique consisted of four steps: (1) extract Ti from ~ 10 mg of calcined samples (after TGA) using 1 mL of H<sub>2</sub>SO<sub>4</sub> for 1 h, (2) add 0.14 mL of H<sub>2</sub>O<sub>2</sub> (30 wt% in H<sub>2</sub>O, Aldrich), (3) dilute the solution to a desired range of Ti concentrations with deionized H<sub>2</sub>O, and (4) measure the concentration of extracted Ti using Ultraviolet-Visible (UV-Vis) spectroscopy (Varian Cary 4000 Bio UV-visible spectrometer) at the absorption of  $\lambda_{\text{max}} = 408$  nm, and calculated the Ti loadings of the catalysts based on the UV-Vis data. Diffuse reflectance UV-Vis spectra were collected on the same Varian Cary 4000 Bio UV-visible spectrometer. We used poly(tetrafluoroethylene) for baseline correction. Solid-state <sup>13</sup>C CP/MAS NMR spectroscopy was performed at the Caltech Solid-State NMR facility

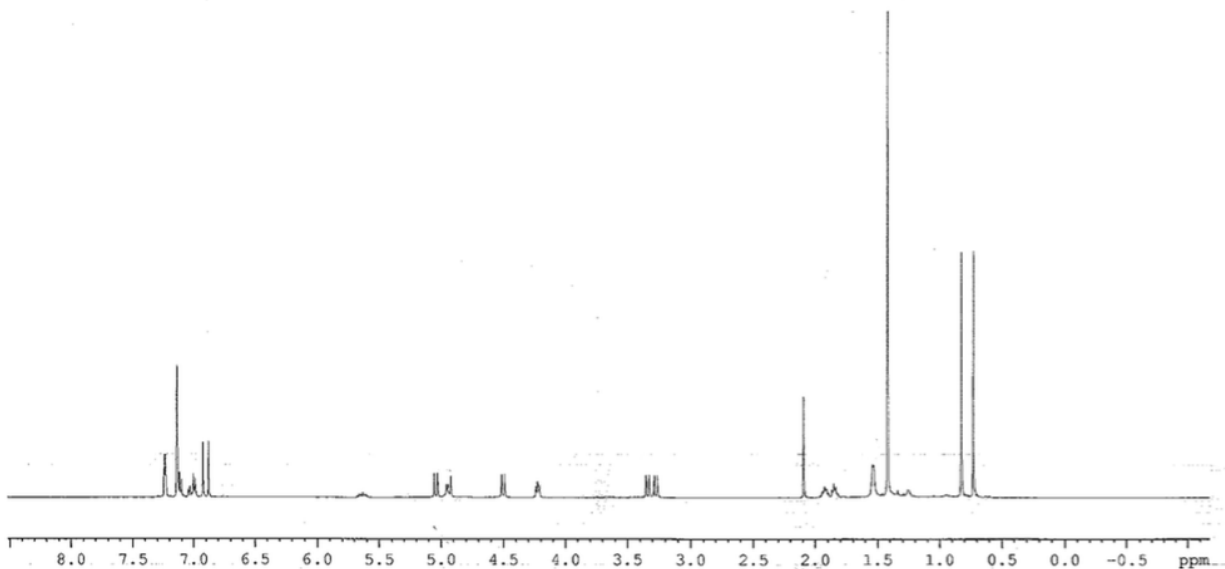
using a Bruker DSX500 spectrometer and a Bruker 4 mm magic angle spinning probe. The spectral frequencies were 125.5 MHz for  $^{13}\text{C}$  nuclei. Typically about 70 mg of samples were packed into zirconia rotors and spun at 8 kHz at ambient condition. Nitrogen physisorption isotherms were measured on a Micromeritics ASAP2020 instrument at 77 K. Prior to measurement, samples were evacuated at 120 °C for 2 h. The pore size distributions were calculated by the non-local density functional (NLDFT) method based on measured nitrogen adsorption data.

#### Synthesis and Grafting of $\text{Ti}(\text{O}^i\text{Pr})$ -Calixarene Complex.

$[\text{Ti}(\text{O}^i\text{Pr})(\text{Methoxycalix})]$  was synthesized and grafted onto  $\text{SiO}_2@800$  according to published procedures.<sup>8</sup> The synthesis of the vinyl-calixarene ligand proceeded as follows. To a stirred suspension of CsF (0.61g, 4 mmol) in 15 mL of DMF, tetra-tert-butyl-calix[4]arene (2.0g, 3.08 mmol) was added. After 20 min at 60 °C, 5-bromo-1-pentene (0.46g, 4.0 mmol) was added to the suspension, and allowed to stir for an additional 18 h. The reaction mixture was poured into 100 mL of deionized  $\text{H}_2\text{O}$  and extracted with chloroform. The chloroform phase was separated and dried over  $\text{Na}_2\text{SO}_4$  overnight. After filtration and evaporation of organic solvent, a white solid was produced. Final purification was performed with column chromatography using a mixture of dichloromethane/n-hexane (1:0.6 v/v) as an eluent ( $R_f$  0.8, 2<sup>nd</sup> spot). A white solid was finally recrystallized using acetonitrile. Yield 47 % (1.04g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  10.19 (s, 1H, OH), 9.59 (s, 2H, OH), 7.08 (s, 2H, ArH), 7.05 (m, 4H, ArH), 6.98 (s, 2H, ArH), 5.95 (m, 1H, CH), 5.21 (m, 1H,  $\text{CH}_2=$ ), 5.08 (m, 1H,  $\text{CH}_2=$ ), 4.34 (d, 2H,  $2J = 13.2$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 4.27

(d, 2H,  $2J = 13.8$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 4.13 (t, 2H,  $3J = 7.2$  Hz,  $\text{OCH}_2$ ), 3.42 (m, 4H,  $\text{ArCH}_2\text{Ar}$ ), 2.46 (m, 2H,  $\text{CH}_2$ ), 2.26 (m, 2H,  $\text{CH}_2$ ), 1.20, 1.21, 1.22 (three s, 36H,  $\text{t-C}_4\text{H}_9$ ).

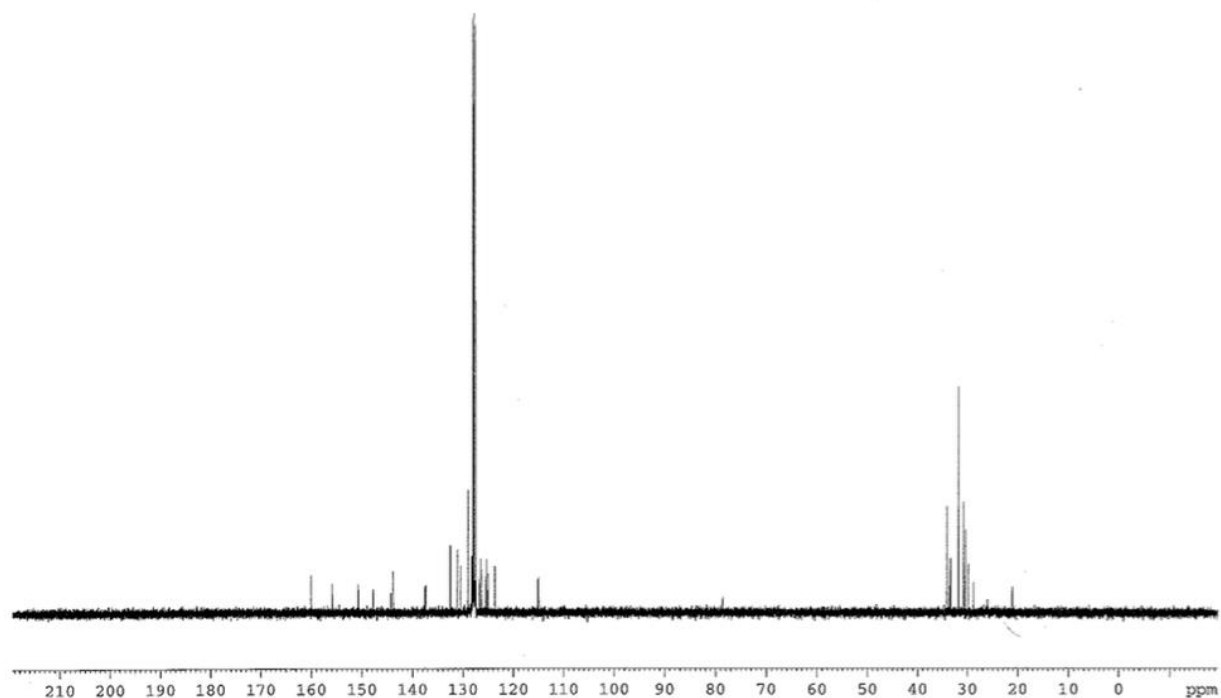
Synthesis of  $[\text{TiO}^i\text{Pr}(\text{Vinylcalix})]$ .  $\text{Ti}(\text{O}^i\text{Pr})_4$  (100.0 mg, 0.35 mmol) was added to a stirred toluene solution (3 mL) of 5,11,17,23-Tetra-tert-butyl-25,26,27-trihydroxy-28-pentenoxycalix[4]arene (252.4 mg, 0.35 mmol). The resulting solution was stirred at  $28^\circ\text{C}$  for 16 h. The resulting solid product,  $[\text{TiO}^i\text{Pr}(\text{Pentenoxycalix})]$ , was recovered by removing the solvent under vacuum. The obtained Ti(IV)-vinyl-calixarene was grafted onto  $\text{SiO}_2@800$  using a similar procedure as previously described for alkyl-substituted calixarenes.<sup>16,17</sup> 1 g of  $\text{SiO}_2@800$  and a magnetic stir bar were first loaded in a 25 mL air-free glass reactor in an air- and moisture-free glovebox. This reaction flask was then transferred to the Schlenk line which was filled with Ar. Ti(IV)-vinyl-calixarene (115 mg, 0.14 mmol) in 8 mL of toluene solution was added to the reactor and the resulting silica slurry was stirred under Ar for 4 h. The solution was then decanted with freshly distilled toluene for at least five times until the supernatant solution is colorless. Finally, the resulting solid product (**IIa**) was recovered by filtration and dried under vacuum at RT overnight and at  $120^\circ\text{C}$  for 1 h.



**Figure S1.**  $^1\text{H}$  NMR spectrum of 5,11,17,23-Tetra-tert-butyl-25,26,27-trihydroxy-28-pentenoxo-Ti(IV)-calix[4]arene ( $\text{TiO}^i\text{Pr}(\text{vinylcalix})$ ) precursor.

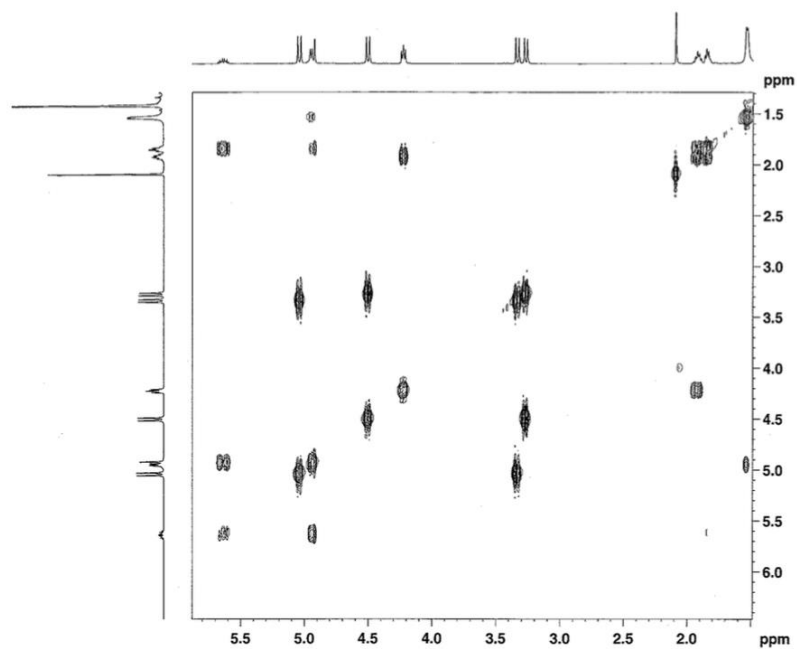
NMR spectra were recorded on either a Bruker AVQ-400 or DRX-500 instrument. Solvent residual peak of benzene (7.16 ppm) in benzene- $d_6$  was used as internal standard.

$^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  7.34 (m, 4H, ArH), 7.02 (s, 2H, ArH), 6.98 (s, 2H, ArH), 5.71 (m, 1H,  $\text{CH}=\text{CH}_2$ ), 5.14 (d, 2H,  $^2J = 12.0$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 5.04 (m, 3H,  $\text{TiOCH}(\text{CH}_3)_2 + \text{CH}=\text{CH}_2$ ), 4.60 (d, 2H,  $^2J = 12.0$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 4.23 (m, 2H,  $\text{OCH}_2$ ), 3.44 (d, 2H,  $^2J = 12.0$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 3.37 (d, 2H,  $^2J = 12.0$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 1.92 (m, 2H,  $\text{CH}_2$ ), 1.86 (m, 2H,  $\text{CH}_2$ ), 1.53 (m, 6H,  $\text{CH}_3\text{CH}$ ), 1.43 (s, 18H, t-Bu), 0.82 (s, 9H, t-Bu), 0.76 (s, 9H, t-Bu).

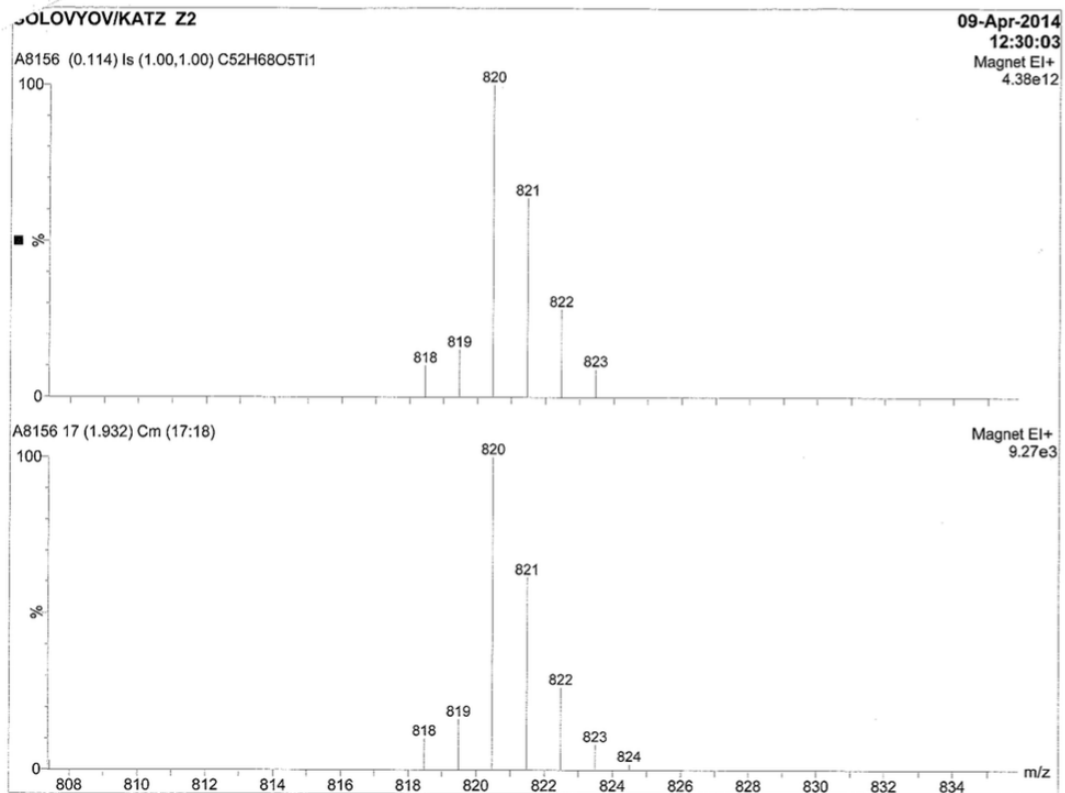
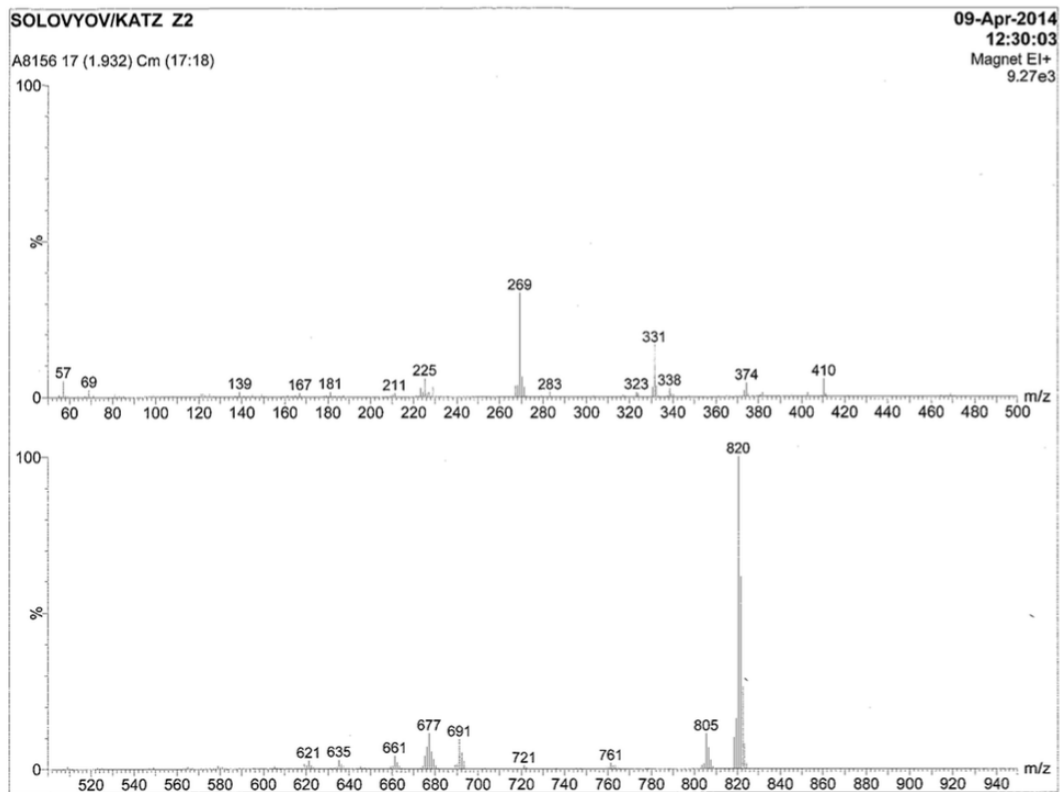


**Figure S2.**  $^{13}\text{C}$  NMR spectrum of 5,11,17,23-Tetra-tert-butyl-25,26,27-trihydroxy-28-pentenoxy-Ti(IV)-calix[4]arene.

$^{13}\text{C}$  NMR (benzene- $d_6$ ):  $\delta$  160.01, 155.87, 150.68, 147.77, 144.21, 143.81, 137.57, 132.47, 131.10, 130.49, 129.02, 128.25, 127.98, 126.80, 126.44, 125.42, 125.38, 125.03, 123.65, 115.08, 78.57, 34.13, 34.10, 33.61, 33.42, 33.34, 31.78, 30.78, 30.40, 29.79, 28.77, 26.04, 21.12.



**Figure S3.** <sup>1</sup>H-<sup>1</sup>H 2D COSY NMR spectrum of 5,11,17,23-Tetra-tert-butyl-25,26,27-trihydroxy-28-pentenoxo-Ti(IV)-calix[4]arene.

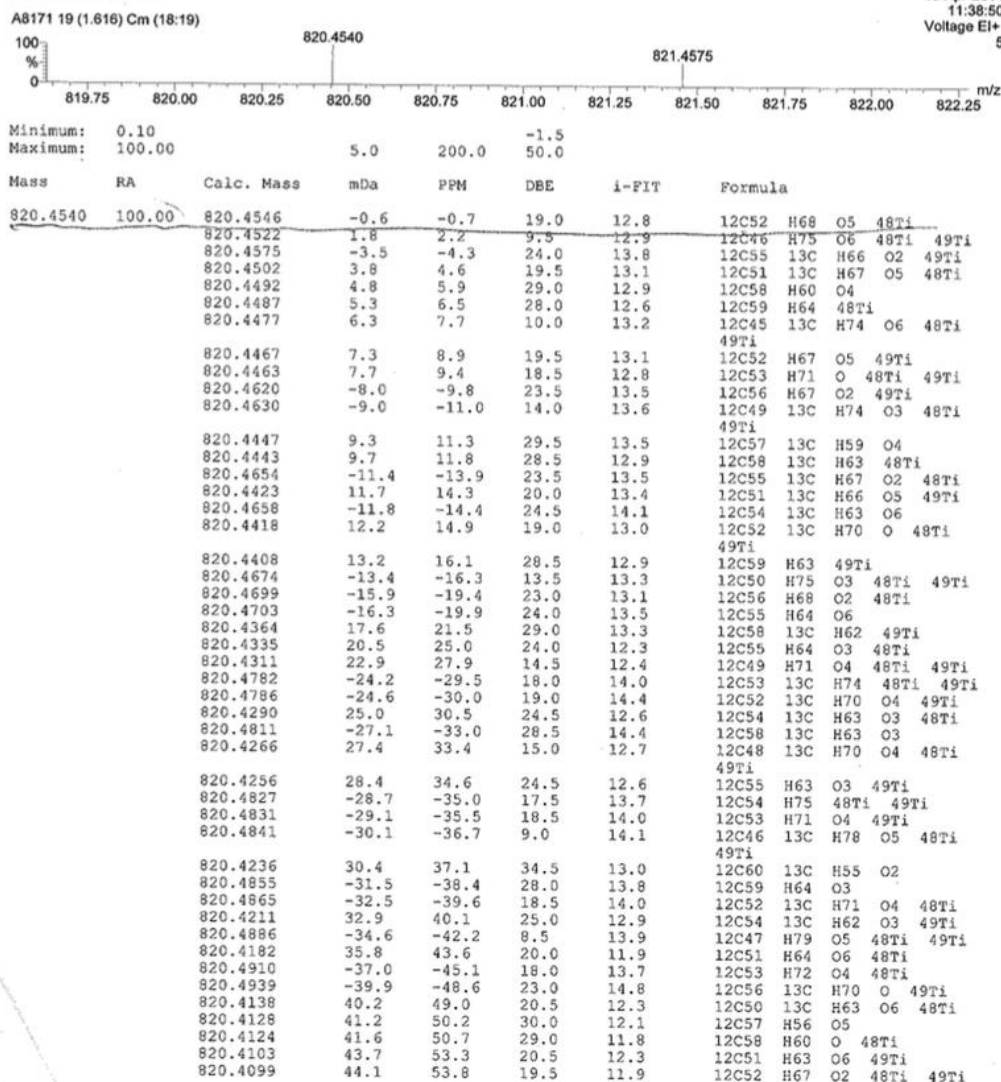




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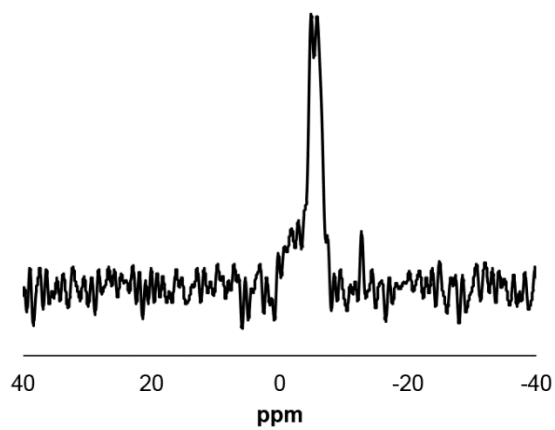
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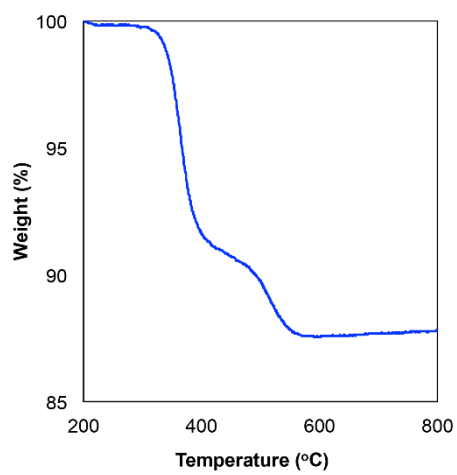


**Figure S4.** High-resolution mass spectrum of 5,11,17,23-Tetra-tert-butyl-25,26,27-trihydroxy-28-pentenoxo-Ti(IV)-calix[4]arene.

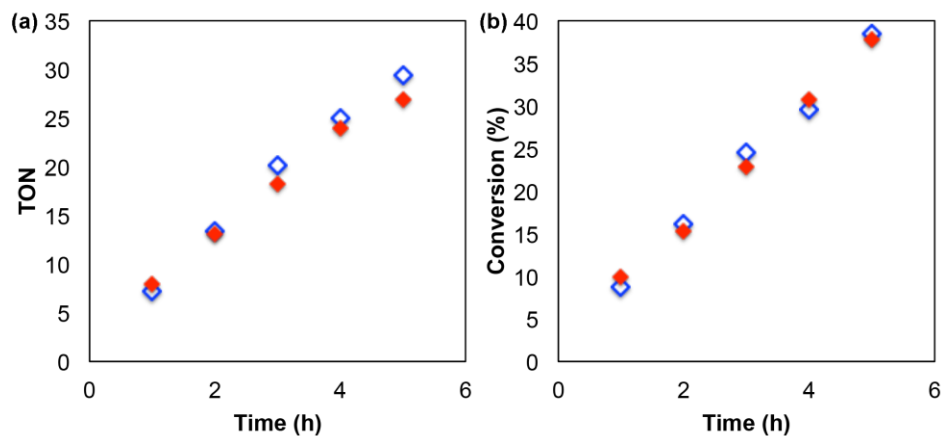
HR EI+ mass spectra were recorded at the UC Berkeley Mass Spectrometry Facility. High resolution EI+ MS calculated for  $C_{52}H_{68}O_5Ti$  was 820.4546, found 820.4540.



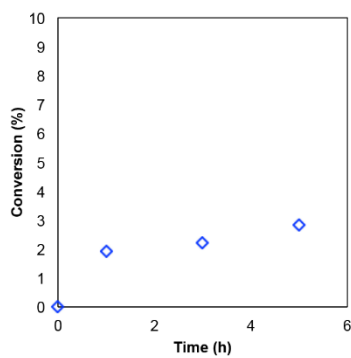
**Figure S5.**  $^{11}\text{B}$  MAS NMR spectrum of **IIc**.



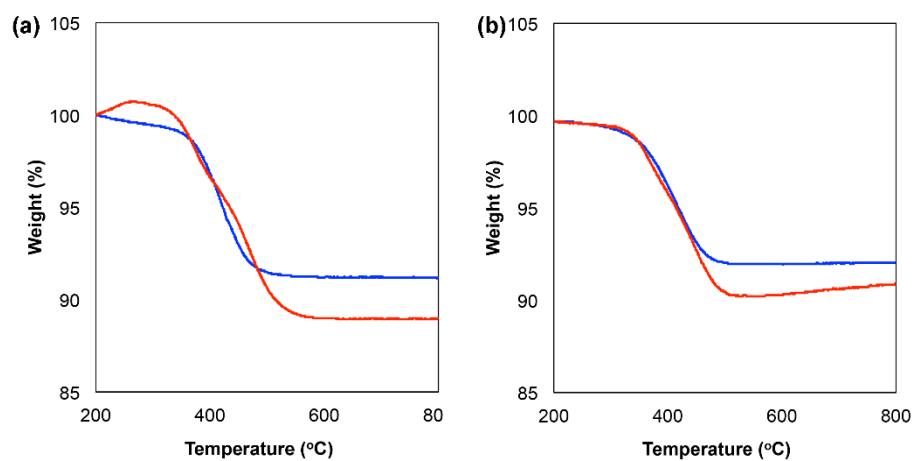
**Figure S6.** TGA of  $\text{SiO}_2@800$  after polymerization with styrene/diisopropenylbenzene.



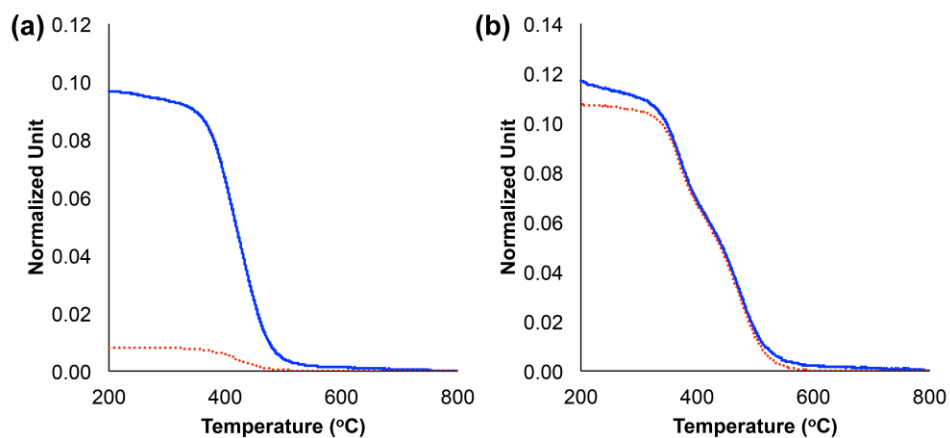
**Figure S7.** Comparison of **IIa** (hollow blue diamond) with **IIc** (solid red diamond) on  $\text{SiO}_2$  support for the 1-octene epoxidation reaction. TON = mol oxidation products / mol Ti.  
Conversion (%) = mol TBHP consumed / mol initial TBHP.



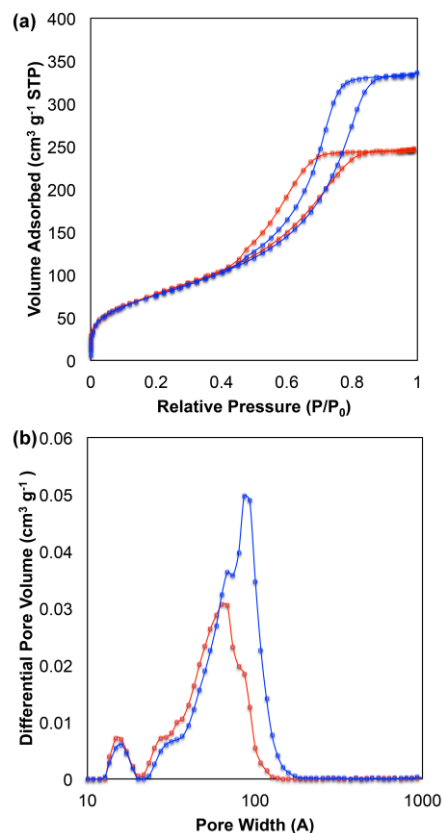
**Figure S8.** 1-octene epoxidation conversions with  $\text{B}(\text{C}_6\text{F}_5)_3$  modified  $\text{SiO}_2@800$ .



**Figure S9.** (a) TGA of **Ia** (blue) and **Ic** (red). (b) TGA of **IIa** (blue) and **IIc** (red).



**Figure S10.** Thermogravimetric analysis of **IIa** and **IIc** before (solid blue line) and after (dashed red line) treated with a mixture of 5 mL isopropanol and 5 mL DI water for 4 h.



**Figure S11.** Nitrogen physisorption isotherms of SiO<sub>2</sub>@800 before (blue) and after (red) polymerization with styrene/diisopropenylbenzene (a), and their pore size distributions calculated from the NLDFT model using desorption isotherms (b).

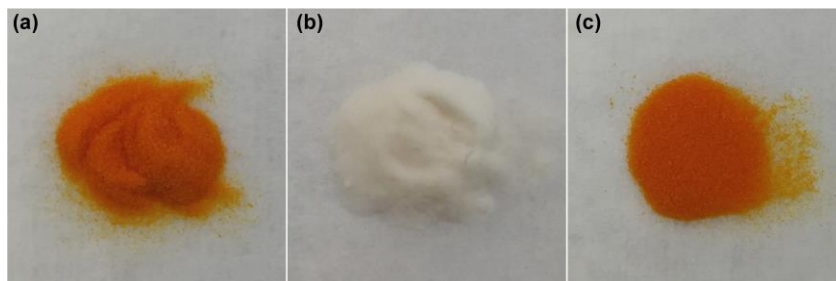
$$\text{TGA Normalized Unit} = \frac{1}{100} \left( \frac{\text{Sample mass @ T}}{\text{Sample mass @ 800 } ^\circ\text{C}} - \frac{\text{Control mass @ T}}{\text{Control mass @ 800 } ^\circ\text{C}} \right)$$

**Figure S12.** TGA normalized unit.

In order to minimize the uncertainty brought by organic adsorption on silica surface, we normalized TGA units following the equation shown above (Fig. S11). The control material refers to a blank silica support that has been dehydroxylated at 800 °C, SiO<sub>2</sub>@800, which has no calixarene ligand on the surface. We treat this control sample under the same hydrolytic stress

test conditions mentioned in the experimental section (flow or batch leaching tests) to allow for chemisorption of any protic species as alkoxides on this silica, as would occur in a real catalyst sample.

Sample mass at certain temperature (T) was divided by the sample mass at 800 °C. This results in a relative weight that is referenced to bone-dry silica – a common basis. We did the same calculation for the control sample, where the control mass at certain temperature (T) was divided by the control mass at 800 °C. We then take the difference between these two values and divide it by 100. This yields organic content as a percentage of the amount of bone dry silica in the sample – corrected for any chemisorption that may occur from the protic species in the leaching stress-test solvent.



**Figure S13.** Pictures of catalyst (a) **Ia**, (b) **Ial** and (c) **Icl**.